References

Surface modification by plasma immersion ion processing

K.C. Walter[a], D.H. Lee[a], X.M. He[a], N.P. Baker[a], M. Nastasi[b], C.P. Munson[c], W.K. Scarborough[b], M. Tuszewski[c], and B.P. Wood[c]

[a]Los Alamos National Laboratory, MS-K762, Los Alamos NM 87545
[b]Los Alamos National Laboratory, MS-K765, Los Alamos NM 87545
[c]Los Alamos National Laboratory, MS-E526, Los Alamos NM 87545

ABSTRACT

Los Alamos National Laboratory is actively researching a surface modification technique called plasma immersion ion processing (PIIP). PIIP is the latest innovation of the plasma source ion implantation (PSII) approach to surface modification. Like PSII, PIIP allows the modification of large areas (many m^2) and non-planar surface geometries, however PIIP is primarily a coating deposition technology rather than solely an ion implantation technology. PIIP utilizes a pulsed-bias on a target to extract ions out of plasma for ion implantation (>10 kV) and coating deposition (<10 kV). Plasmas can be made by capacitive or inductive radio frequency sources or by initiating a glow discharge during each pulse of high voltage. Plasmas of hydrocarbon gases have been used to deposit adherent diamond-like carbon (DLC) coatings on a variety of ferrous and non-ferrous materials. Instead of sputter depositing interlayers to improve the adhesion of DLC, PIIP uses ion implantation to create a graded interface between the metallic substrate and the DLC coating. Demonstrating the scaleability of PIIP, a 3 m^2 area has been simultaneously coated with an adherent DLC coating approximately 7 μm thick. Plasmas of diborane and acetylene mixtures are being used to develop deposition processes for boron-carbide coatings. Through the use of organometallics and inorganic gases, other coatings are possible. The PIIP deposition conditions, composition and tribological properties of DLC and boron-carbide coatings will be highlighted.

Keywords: tribology, coating, diamond-like carbon, boron-carbide, PIIP, PSII

1. INTRODUCTION

Since development of plasma source ion implantation (PSII) began at the University of Wisconsin-Madison in 1986[1], interest in this versatile surface modification technique has continued to increase. The total number of operational PSII facilities (Fig. 1) has been doubling every two years and is now approaching 50, with some locations having more than one operational system. Between 1986 and 1993, a majority of operational PSII systems were in the United States. Initial PSII research in the US concentrated on tribological applications, but around 1990 began to include work for semiconductor applications. Australia began PSII research around 1987 and has concentrated on nitrogen implantation of ferrous materials at high temperature. The period of 1991 to 1994 saw the initial operation of almost all of the known systems in Asia. Research interests vary from semiconductor applications in Japan, to surface wetting studies in Korea, to tribological applications in China. More recently, Germany, France, Great Britain, and Finland have established PSII research programs for both tribological and semiconductor applications. Along with the increase in PSII research, the number of variations on the original PSII theme, which was once limited to ion implantation, has also grown to include coating deposition and interface engineering.

Within the US, PSII research initially concentrated on nitrogen implantation to improve the wear resistance of metals[2], but later evolved to include research on increasing the wear and corrosion resistance of Ti-6Al-4V[3] and other ion implantation processes for the semiconductor industry[4-5]. Despite promising laboratory results in the tribological and corrosion fields, potential applications of PSII were still limited by the inherent shallowness of ion implanted surface layers (<200 nm). In response, PSII research began to combine ion implantation with coating deposition[6]. It was also noted that hydrocarbon gases could be utilized in a PSII process to produce hydrogenated diamond-like carbon (DLC) coatings[7]. In an effort to improve the adhesion of DLC coatings on metals, PSII has been utilized to create a compositionally graded interface[8] between DLC and many different metals[9]. The successful use of PSII to coat ~3 m^2 with DLC and implant ~4 m^2 with nitrogen has been demonstrated[10]. This paper will highlight some of the recent efforts to use PSII to improve the wear resistance of electrodeposited hard Cr coatings through nitrogen implantation[11], for DLC deposition[9,12-13], for the deposition of adherent coatings of erbia onto stainless steel[14], and for the use of diborane and acetylene to deposit boron-carbide coatings[11].

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Fig. 1. A world map showing the known locations of facilities actively doing PSII research in 1997.

2. EXPERIMENTAL

2.1 Coating deposition for liquid metal containment

The preferred method for making a metal ion plasma for PIIP is to use a cathodic, or vacuum, arc source[14]. As an example, an erbium cathode was used to make an erbium plasma consisting of Er^{+2} and Er^{+3} ions. Pulse-biasing the 304L stainless steel target at -20 kV, resulted in an effective implantation bias of -40 to -60 kV and produced a compositionally graded interface. Adding 0.03 Pa of oxygen (O_2) into the vacuum chamber, and lowering the magnitude of the pulsed bias, allows deposition of a Er_2O_3 coating. X-ray Photoelectron Spectroscopy (XPS) depth profiles were obtained by intermittently sputtering the surface of the sample with argon and taking spectra for specified elements in between the sputtering steps. The spectra were combined, using established data analysis techniques and tabulated sensitivity factors, to produce a concentration depth profile. The adhesion of the erbia coating to 304L was tested by depositing the coating into a shallow cup and using a Charpy impact tester to dent the cup inside out, putting the coating in tension. Scanning electron microscopy (SEM) was used to determine the microstructure of the coating on the dented surface.

2.2 Adherent DLC coatings on metals

A PIIP process that has been described in detail elsewhere[8-9] has been used to deposit adherent DLC coatings on many metals ranging from Mg to W. The importance of the ion implantation step in promoting DLC adhesion was measured by depositing identical coatings on two samples, one with an ion implantation treatment, and one without. The ion implantation step utilized a PSII process, 0.07 Pa (0.5 mTorr) of methane (CH_4) gas, a 50 kV pulse bias, and a incident dose of ~$5x10^{17}$ ions/cm^2. After implantation, the surface was briefly sputter cleaned to remove any graphitic C-layer that could interfere with coating adhesion. DLC deposition was accomplished by filling the chamber with 0.04-0.05 Pa of C_2H_2, pulse-biasing the targets to –1.5 kV for 30 μs at 5 kHz for 3.5 hours. Pulsed-glow discharge generation of the plasma was assisted by operating a capacitive rf antenna at 13.56 MHz and about 300 W. The adhesion strength of coatings was measured in tension using the Sebastian® II stud pull test.

2.3 DLC coating deposition using an rf-inductive plasma

A PIIP process that uses an inductive rf-plasma of a mixture of argon (Ar) and acetylene (C_2H_2) gases has been used to deposit DLC coatings on a variety of substrates[12-13]. The process is scaleable to any size vacuum chamber. The plasma

generation approach is based on two sources composed of copper tube coils enclosed in alumina tubes that are inserted into the chamber[15]. Each of the coils is powered by a 3 kW, 0.46 GHz rf source. The gas mixture can be easily varied, but for this work, the Ar:C_2H_2 mixture was either 2:1 or 5:1. The total pressure was either 0.04 or 0.53 Pa during deposition. A pulsed glow discharge plasma from a 2.7 Pa mixture of diborane (B_2H_6) and C_2H_2 was also used in an effort to study the effect of B-doping on the optical properties of DLC[13]. Coating hardness was measured using a NanoIndenter II and the continuous stiffness option. Reported hardness values were measured at a depth of 50 nm. The curvature of a Si beam was measured using a laser reflection method before and after deposition and the stress was calculated using Stoney's equation[16]. Coating composition was measured using Rutherford Backscattering Spectrometry (RBS) and Elastic Recoil Detection (ERD). Coatings with useful properties were typically comprised of 3-4 at% Ar, 25-30 at% H, and 65-70 at% C. The optical transmittance of DLC coatings on PMMA was measured in the visible wavelengths from 200 to 800 nm.

2.4 Deposition of boron-carbide coatings

As an example of how different gases can be easily combined for coating deposition studies, a PIIP process using a mixture of 15% diborane (B_2H_6) diluted in helium (He) and acetylene (C_2H_2) has been used to deposit boron-carbide coatings[11]. A plasma was generated from the gas mixture by applying a pulsed voltage to the sample stage. A plasma is generated spontaneously during the pulse through a glow discharge process. The pulsed bias magnitude was 4 kV, the pulse width was 30 μs, and the pulse frequency was 4 kHz. Silicon (Si) and molybdenum (Mo) substrates were coated at room temperature. Ion beam analysis techniques were used to determine the coating composition. The hardness and modulus of the coatings were measured at ten locations using a NanoIndenter® II operated in the continuous stiffness mode. Pin-on-disk wear tests were performed on the coated Si substrates using a smooth, 6 mm diameter 52100 ball, 50% relative humidity, loads from 0.2 to 0.4 N, a Hertzian contact stress from 360 to 460 MPa, 120 rpm, and a track diameter of 3 mm. The coefficient of friction was calculated by measuring the tangential force on the pin through a load cell.

3. RESULTS AND DISCUSSION

3.1 Coating deposition for liquid metal containment

The XPS depth profile for erbia coated 304L is shown in Fig. 2. The XPS spectra for erbium (not shown) indicated the element is completely bound as Er_2O_3 and the complete absence of erbium metal. There was ~12at% carbon at the interface (not shown in the profile for clarity) that resulted from insufficient sputter cleaning before processing began. The profile indicates diffusion of iron and chromium into the erbia coating, but no diffusion of nickel is indicated. Although nickel and iron form intermetallics with erbium, it is speculated that the higher enthalpies of formation for the iron and chromium-oxides drive the transport of iron and chromium, but not nickel. The profile also indicates the presence of erbium and oxygen

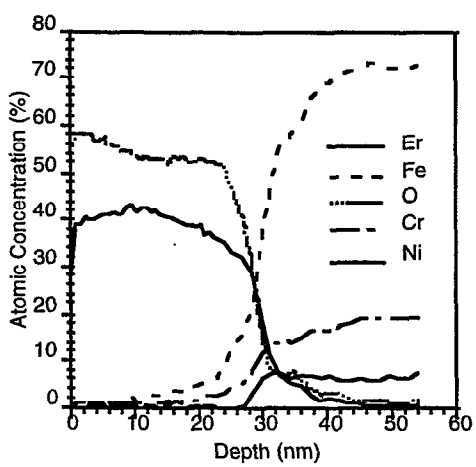

Fig. 2. XPS depth profile of the erbia-steel interface.

beneath the steel surface and is indicative of the high voltage implantation of these elements. The implantation depths of 40 keV and 60 keV erbium ions into iron are about 10 and 12 nm, respectively. The implantation depth of 10 keV O_2^+ in iron is

about 11 nm. These depths are consistent with the depths observed in Fig. 2. The combined effects of the implantation of erbium and oxygen into 304L, and the transport of iron and chromium into the oxide coating result in an interface ~20 nm in width.

An example of the high adherence achievable with the PIIP process can be seen in Fig. 3, which shows an SEM image of a 3 μm erbia coating implanted and deposited upon the inside of a shallow 304L stainless steel cup. The cup was subsequently dented inside out with a 16 mm diameter Charpy Impactor. The erbia coating has cracked, due to the tensile stresses imposed by substrate deformation, but has not delaminated. Such a cracked coating is still useful for containing reactive molten metals if the coating is not wetted by the molten metal.

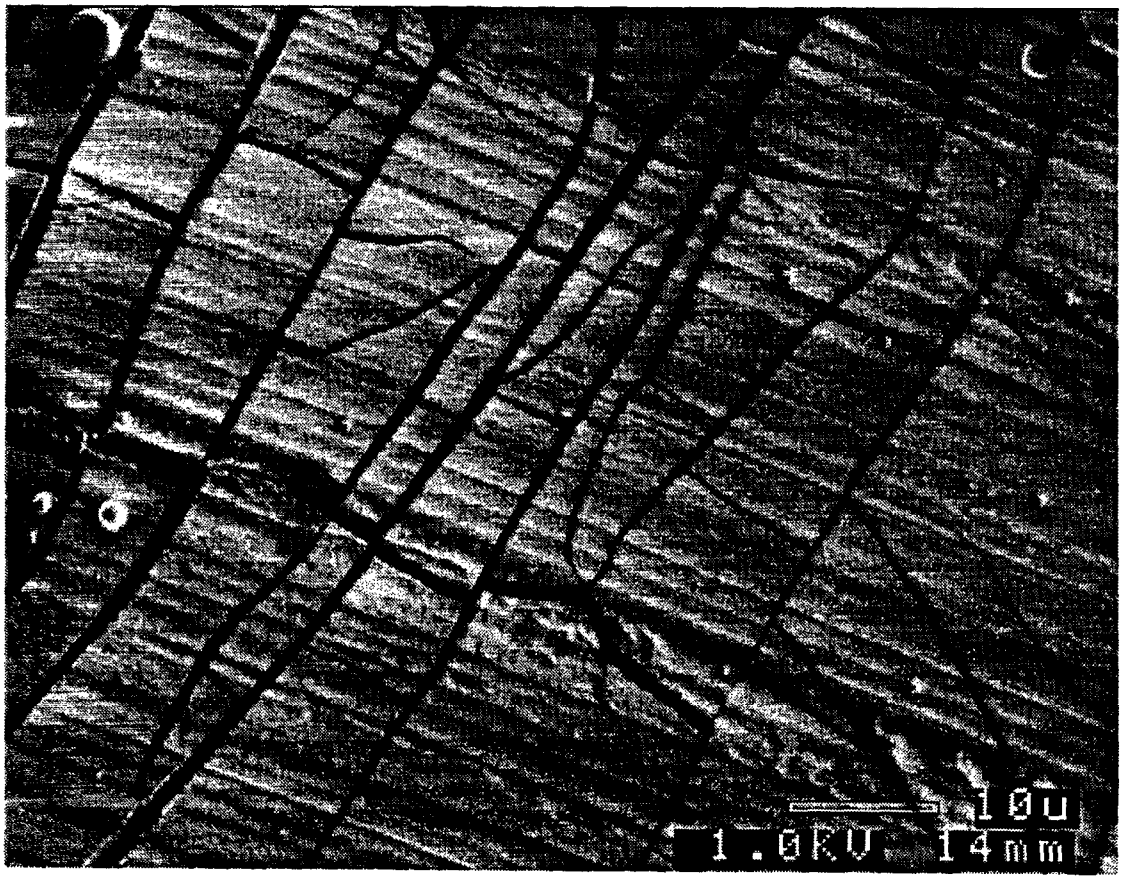

Fig. 3. A 3 μm erbia coating on 304L stainless steel which has been dented inside out with a Charpy Impactor. No delamination is observed.

3.2 Adherent DLC coatings on metals

Although many metals were included in the study[9], only the results for W will be highlighted here. The adhesion strength of DLC-coated W without C-implantation before coating varied from 11 to 39 MPa. The DLC-coating on W that had been implanted with C prior to DLC deposition had an adhesion strength of 42 to 46 MPa. SEM micrographs of one test on each of the samples is shown in Fig. 4. The adhesion results indicate that the creation of a compositionally graded interface improves the adhesion of DLC coatings to W. The SEM micrographs confirm the epoxy generally forms the weakest interface for the adhesion test. Therefore, the reported adhesion strengths for the C-implanted and DLC coated W (46 MPa) can be viewed as a minimum estimate of the coating adhesion strength. Similar results for other metals, even metals that do not readily form carbides, were also seen and illustrates the value of using ion implantation to create graded interfaces rather than thermal processes that depend on diffusion or carbide formation.

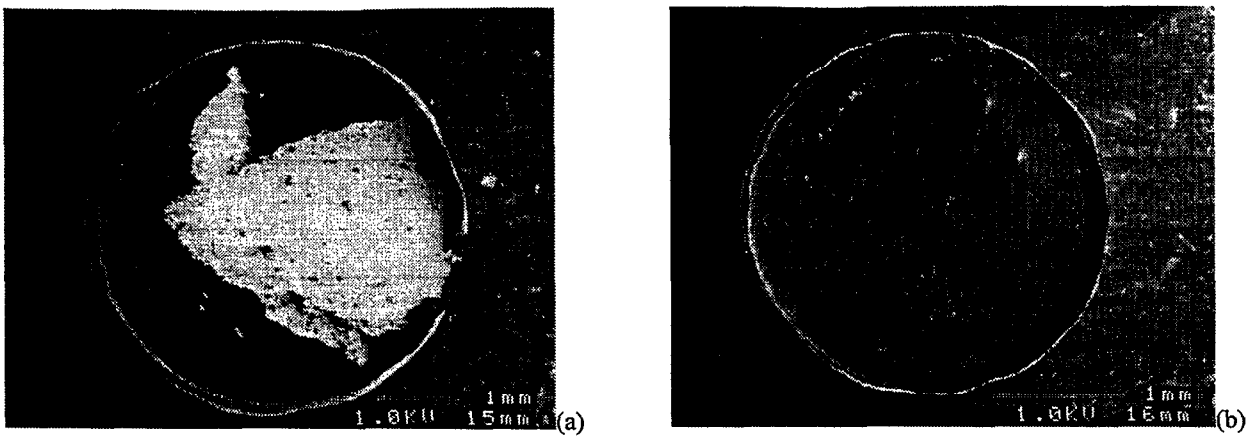

Fig. 4. SEM micrographs of DLC coated W. (a) Without carbon implantation, the DLC coating is partially removed; (b) with carbon implantation, the DLC coating is more adherent and no area of delamination is observed.

3.3 DLC coating deposition using an rf-inductive plasma

The hardness and compressive stress of DLC coatings deposited at different gas pressures and pulse-bias conditions are shown in Fig. 5. A negative pulse-bias of 150 V and a gas pressure of 0.04 GPa (Ar:C_2H_2 of 2:1) were used to deposit coatings with the highest hardness and compressive stress. The coating thickness varied between 100 and 300 nm. Assuming the hydrocarbon ion species is $C_2H_2^+$, the carbon atom energy for a pulse-bias of –150 V and a plasma potential of -23 V is about 80 eV. This is in good agreement with other energetic deposition methods that use a carbon ion energy of 100 eV to get the best quality DLC[17-18]. The optical transmittance of equivalent coatings deposited on poly methyl methacrylate (PMMA) is shown in Fig. 6. The transmittance can be improved by adding diborane, instead of Ar, to the gas mixture and depositing at a higher pressure and negative pulse-bias. This work, while still in the research stage, demonstrates the utility and potential of PIIP for the deposition of adherent, scratch resistant, and transparent coatings for a variety of materials.

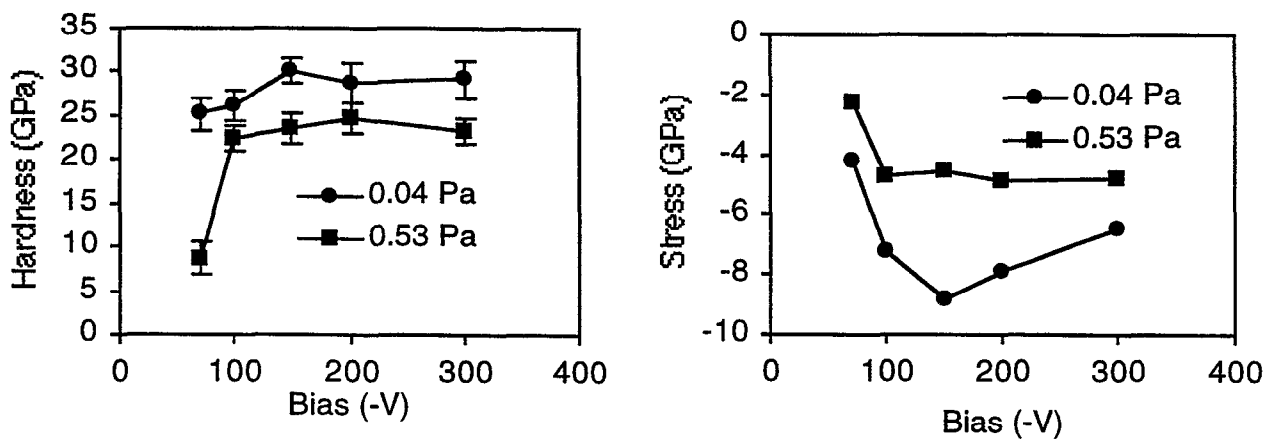

Fig. 5. Hardness and stress data for DLC coatings deposited at two different gas pressures, a constant gas mixture of 2:1 Ar:C_2H_2, and at various negative pulse-biases.

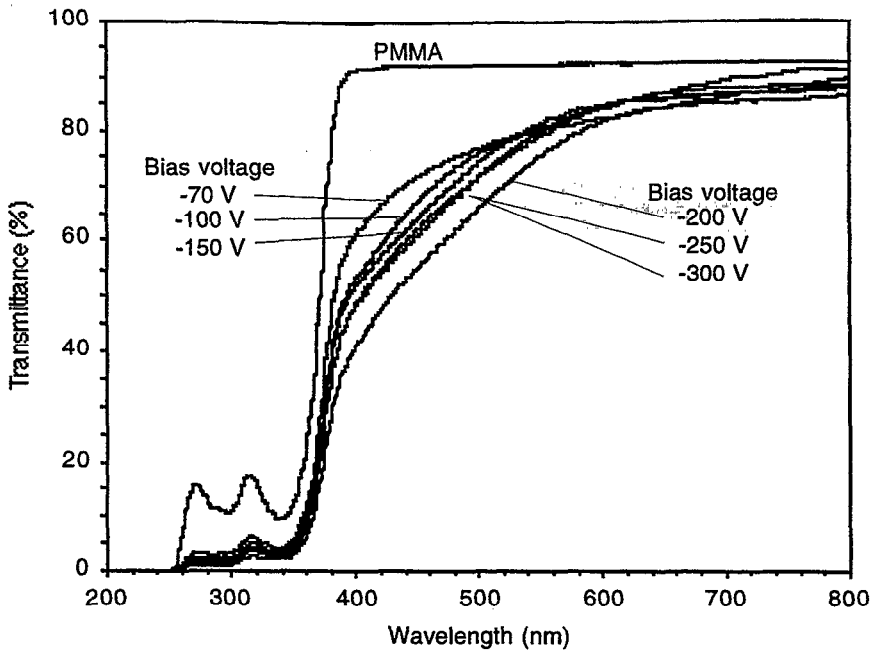

Fig. 6. The optical transmittance of DLC coatings on PMMA as a function of negative pulse-bias. The gas mixture was 5:1 Ar: C_2H_2, the gas pressure was 0.53 Pa, and the coating thickness was held constant at ~220 nm.

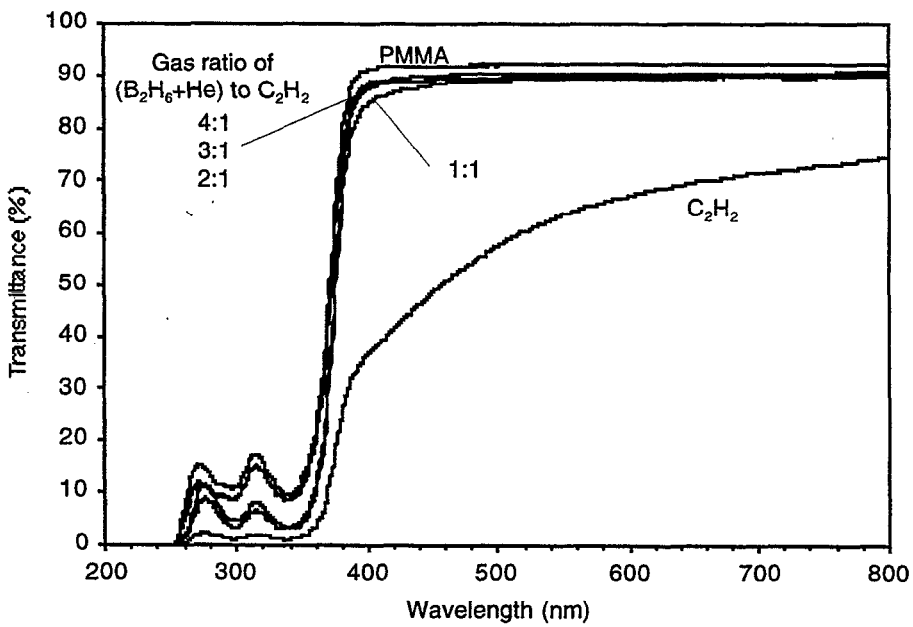

Fig. 7. The optical transmittance of DLC coatings on PMMA deposited at –2 kV pulse-bias, a gas pressure of 2.7 Pa, and various B_2H_6(He):C_2H_2 ratios. The coating thickness varied from 200-250 nm.

3.4 Boron-carbide coatings

The boron to carbon ratios of the coatings are shown in Fig. 8. The data indicate that small changes in the gas mixture can have a large affect on the coating composition. The hydrogen content of the coatings was between 25 and 40 at%. Oxygen content was always less than 3 at%. The deposition rate varied from 0.1 to 0.4 μm/hour. The coating is believed to be amorphous. The hardness of the coatings is between 12 and 14 GPa and the elastic modulii ranged between 110 and 150 GPa and these values did not vary considerably with coating composition. Fig. 9 shows the coefficient of friction for three coatings with different compositions. Unlike the hardness and modulus, the tribological behavior of the coatings depends greatly on coating composition. As seen in the figure, the coefficient of friction increases as the coating is worn away and the ruby ball interacts with the Si substrate. Coatings with greater wear resistance have a lower coefficient of friction for a greater number of wear cycles. The coating with the greatest carbon content, B/C = 2.2, has the best wear resistance. Fig. 10 shows the coefficient of friction for the coating with B/C=2.2 for different contact stresses. Note the marked difference between the friction traces when changing the contact stress ~10% from 358 to 391 MPa.

These initial experiments prove boron-carbide coatings can be deposited by a PIIP process. As shown in Fig. 8, the coating composition is highly dependent on the diborane content in the gas. The processing window is thus very narrow and there is concern that large scale processing may be difficult without the use of expensive process controls. While other researchers have used other gas combinations to produce boron-carbide coatings[19,20], this work represents the only known attempt to use diborane and acetylene mixtures to deposit boron-carbide. Secondly, the coating hardness of 12-14 GPa is higher than reported in another study[20]. In the future, research efforts will be directed at reducing the hydrogen concentration in, and improving the crystallinity of, these B-C coatings.

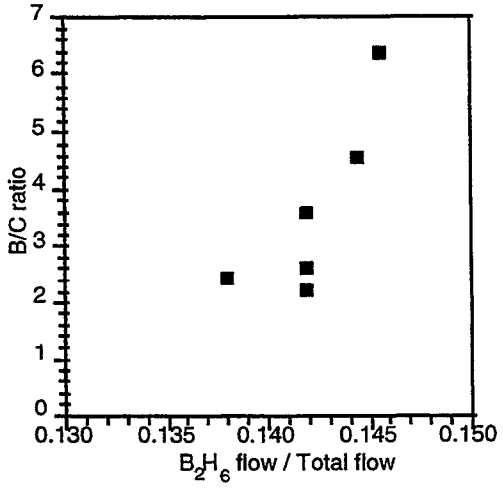

Fig. 8. The boron to carbon ration in the boron-carbide coatings as a function of gas composition. The B/C ratio varies below and above the target of B/C=4 (for B_4C) over a narrow range of gas composition.

4. SUMMARY

PSII is a technology that is continuing to evolve to meet the demands of the surface modification industry for improved wear resistance as well as liquid metal containment. The most recent PSII-related technology to be demonstrated is PIIP, which includes all the advantageous attributes of PSII, but allows for interface engineering and coating deposition. Treatment of areas exceeding a few m^2 has been demonstrated for both ion implantation and coating deposition. To date, only a few of the many possible gas combinations have been used in PIIP. These many possible gas combinations, in conjunction with the many choices for plasma generation, make PIIP a versatile surface modification process with great potential.

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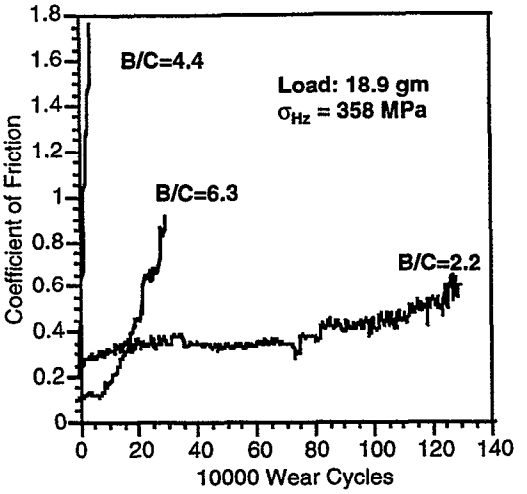

Fig. 9. Coefficient of friction for coatings containing 12 at% carbon (B/C=4.4), 8 at% carbon (B/C=6.3), and 19 at% C (B/C=2.2).

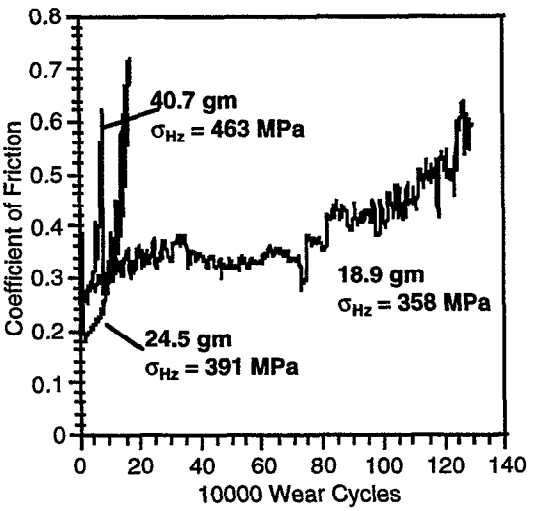

Fig. 10. Coefficient of friction for the coating with B/C=2.2 measured for different contact stresses.

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